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A CALORIMETRIC DETERMINATION OF THE ENTHALPY OF FORMATION AND A DESCRIPTION OF THE DEFECT STRUCTURE OF THE ORDERED BETA-PHASE /Ni, Cu//1-x/ Al/x/

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16. Abstract

In order to describe thermodynamically the defect structure of an ordered B-Hume-Rothery phase, the heat of formation of $(Ni,Cu)_{1-x}Al_x$ was measured at 1100 K as a function of concentration in the range $x_{Al} = 0.4$ and 0.55 for three substitution ratios $x_{Ni}/x_{Cu} = \infty$; 11; 5. The heat of formation of the NiAl β-phase is strongly negative. For the stoichiometric composition it is -72.2 kJ/g-atom. On both the nickel-rich side and the aluminum-rich side the magnitude of the enthalpy of formation decreases linearly with concentration. Substitution of nickel for copper decreases the magnitude of the enthalpy of formation over the entire homogeneity range for the phase $(Ni,Cu)_{1-x}Al_x$. The curve for the enthalpy of formation as well as the literature values for the chemical potential of aluminum are described with great accuracy by the disorder model of Wagner-Schottky.

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The properties of intermetallic phases are strongly influenced by the disorder structure. The disorder equilibrium, in its dependence on the concentration and temperature, should be described as accurately as possible by thermodynamic models with a few energy parameters.

Wagner and Schottky [1] have developed a disorder model for intermetallic phases with largely ordered atomic distribution. Three basic types of disorder are distinguished: interstitial, vacancy, and substitution types. Concentration-independent energies for the individual disorder elements is a prerequisite for this model. the validity range of the model is limited by its authors, therefore, to small vacancy concentrations and as a result to small deviations from stoichiometry.

Refined models, which also consider concentration-dependence of the energies and entropies of the individual lattice elements have been published by Bonnier, Mathieu, Durand and Allibert [2-4] under the concept of "atome entouré", and by Lupis and Elliot [5] as "central atom". The experimental testing of the model, therefore, essentially requires measurement of the concentration dependence of the energy parameters.

One common structure type of intermetallic phases with a wide homogeneity range is the cubic B2 or CsCl type, which consists of two cubic-primitive sublattices displaced by the amount (½,½,½). Among the representatives of this B2 type, it has been shown by X-ray analysis combined with density measurements, for CoAl [6],

NiAl [7] and PdAl [8] that essentially only two disorder types occur. T-metal antistructure atoms occur on the T-metal-rich side, and T-metal vacancies occur on the B-metal-rich side. [1]

There are experimental values on the course of the activity as a function of the concentration for B2 structures, particularly for CoAl [9], NiAl [10] and PdAl [8]. In the nickel-aluminum system there are some measurements of the enthalpy of formation by Kubaschevski [11], and by Dannöhl especially for the ß case.

Libovitz [13,14] compares the B-metal activities as functions of the concentration with the activity curve calculated according to an expanded Wagner-Schottky model. Deviations of the measurements from the model are considered by Jacobi and Engell [16] by means separate treatment of the energy state of the electrons.

The free enthalpies derived from the activities or the vacancy concentrations can be separated into enthalpy and entropy only with very low accuracy. The measurements also exhibit distinct scattering. Therefore, independent enthalpy measurements are absolutely necessary in order to be able to make any statement about the concentration dependence of the enthalpy term. Such an independent determination of the enthalpy is possible only through calorimetric measurement. The most accurate values for enthalpy of formation as a function of the concentration $H^{M}_{(x)}$ are those reported by Dannöhl and Lukas [12] for the ß phase NiAl. These values show that the reproducibility of $H^{M}_{(x)}$ must be improved by at least a factor of 10 in

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1 Translator's Note: T-metal may mean 'transition metal'.

order to make reliable statements about the first and econd derivatives of H" with respect to the concentration, x. A high-temperature calorimeter with a measurement reproducibility of at least 1% was designed for accurate determination of the concentration dependence.

The Calorimeter / 99

The calorimeter was designed as an isoperibolic heat-flow differential solution calorimeter [17] because of three main requirements for the measurement - defined initial and final states, same order of magnitude of measurements and desired quantities, and insensitivity to environmental disturbances.

Figure 1 shows the measuring principle, and the schematic design of the calorimeter in a longitudinal section. Two equal calorimeters, each containing a metal bath and a sample, are mounted in one large block as the common environment. To determine the heat of solution, one of the samples is placed in the metal bath, while the other calorimeter serves as the reference state. The heat of transformation on dissolution of the sample is recorded as a temperature difference - time curve. A total of four calorimeters are inserted in large holes in the block. Four differential thermopiles are arranged between the calorimeters so that the temperature difference is recorded between each pair of adjacent calorimeters.

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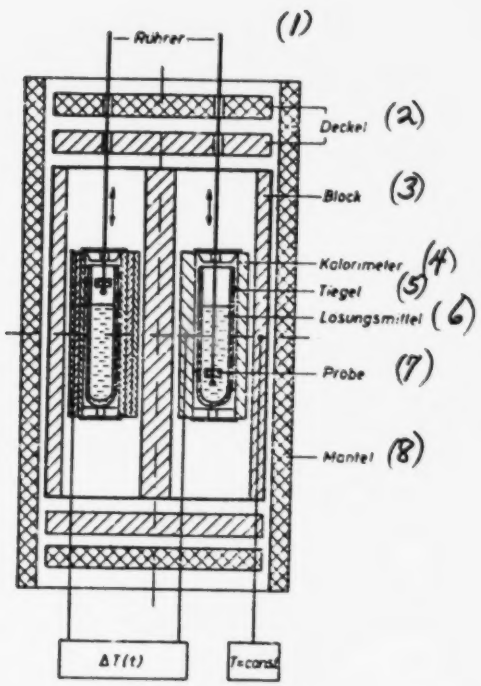

Figure 1. Schematic diagram of the heat flow differential calorimeter.

1. Stirrers
2. Covers
3. Block
4. Calorimeter
5. Crucible
6. Solvent
7. Sample
8. Jacket

covers connect to the block at the top with two more at As the longitudinal section in Figure 1 also shows, two the bottom, and a cylindrical jacket surrounds the block

coaxially. The block, the covers, and the jacket are heated so that the block and inner cover (singly hatched) form the constant-temperature environment for the calcrimeter. The outer cover and the jacket (cross-hatched) are the external environment which gives off most of the heating power.

The block (of nickel, like all the other parts) is controlled at a constant temperature by means of a highly stable set-point potential which serves as a reference temperature for all the other heaters. Both the inner covers are secondarily controlled to have the smallest possible constant temperature difference from the block temperature. Likewise, the outer covers and the jacket are controlled with a constant temperature difference below the temperature of the internal environment (block and inner cover).

The individual control circuits are of essentially the same design. Each control circuit consists of the individual components: thermocouple, comparison thermocouple thermostat [18] and galvanometer amplifier. Connected to this are a proportional integral differential controller (PID controller) which provides the heating power, floated from ground, through an isolation transformer to the heating coils.

Eight independent delta T(t) curves are recorded as measurement signals. Four are temperature differences between adjacent calorimeters, and four are temperature differences between the individual calorimeters and the block. The measurement signals originating at the thermopiles are amplified by galvanometer amplifiers and

recorded on a multi-channel recorder. The temperature difference - time integral is proportional to the heat converted in the calorimeter. The proportionality factor is determined by electrical calibration.

he calorimeter works over a temperature range of 650 to about 1300 K under protective gas or in vacuum. The lower limit is determined by the Curie temperature of nickel (631 K), and the upper limit by the insulation resistance of the thermocouples. That drops off sharply with rising temperature because of the increasing vaporization of the insulating tubes. Below the Curie temperature of nickel, in the range from 400 to 600 K the measurement can only be done in protective gas because the time constants of the control loops are too great in vacuum. The optimal measuring range is from 800 to 1200 K.

At the temperature of 1100 K selected for this investigation the constancy of the baseline of the delta-T curves is better than 5 x 10^{-4} K/d. For the duration of a single measurement, 1 to 3 hours, the constancy is 10^{-4} K. Therefore heat conversions of 1 to 2 J can be measured with accuracy of ±20%. With the time constants given, this gives a measuring duration of about 1 hour. From this we can estimate a mean temperature change of 4-x-10^{-4} K and a mean heat flux of 0.4 mW. The upper limit of the measurement effect is limited only by the fact that the reaction must not be too vigorous because solvent would spray out of the crucibles.

Performance of the Experiment

NiAl samples were prepared between 40 and 54 atom-percent aluminum. (Ni,Cu)Al samples were prepared in the range of solubility of copper in β-NiAl investigated by Bradley and Lipson [19]. For the copper-containing samples, two sections with constant Ni/Cu were selected, one section ith Ni/Cu = 11 and one with Ni/Cu = 5. By this choice of sections, it is possible to achieve a constant concentration of the final solution which is dissolved in aluminum.

The alloys were melted directly from the elements in a vacuum induction furnace. The elements had the following purities: Al, 99.99%; Ni, 99.7%; and Cu, 99.9%. The vacuum furnace was filled with pure argon at 20 Torr to prevent evaporation loss of the aluminum in particular. 80 to 100 g of alloy was produced each time, in order to achieve good mixing of the melts. The melt was cast in a copper mold. The difference between the weight in and the weight out was always less than 50 mg. If this loss is assigned completely to the aluminum, as the element with the highest vapor pressure, the error amounts to about 0.05 weight percent, or about 0.1 atom-% uncertainty in the sample composition.

The cylindrical samples were next annealed for ten /100 days at 1100°C under protective gas, held for another 5 days at 800°C, the later measuring temperature, and then quickly cooled in the oven to room temperature.

Because of a possible change in surface composition due to differential vaporization rates, the surfaces of the

samples were ground off. Disks weighing about 1 g were cut off with a SiC cutoff wheel. A hole was bored in each of these using a spark erosion machine. The sample was mounted on the stirrer through this hole for the measurement.

The samples and the elements were always dissolved in highest-purity aluminum (99.99%). Thus it is not necessary to determine the enthalpy of solution of one element, aluminum, and this avoids a potential error source. The nickel and copper samples were heated to incandescence in moist hydrogen for reduction immediately before they were installed in the calorimeter. Before the solution process the samples were held at the measuring temperature for at least five hours.

Results

The enthalpy of formation, H^B, is determined from the scheme valid for state functions (Hess' law):

$$\begin{array}{ccc} xA + (1-x)B & \xrightarrow{H^B} & A_xB_{1-x} \\ & {\scriptstyle H^{L,1}} \searrow \quad \nearrow {\scriptstyle H^{L,2}} & \\ & [xA + (1-x)B]_{3L} & \end{array} \qquad (1)$$

so that $H^B = H^{L,1} - H^{L,2}$.

Here $H^{L,1}$ is the enthalpy of solution of the elements, and $H^{L,2}$ is the enthalpy of solution of the compound having the same composition and mass. As the enthalpy of formation of a phase, which is to be determined, is just the difference between its enthalpy of solution and the enthalpies of solution for the elements of which it

consists, it is also necessary to determine the enthalpies of the nickel- and copper-containing aluminum melts as a functin of the composition.

The integral enthalpy of the aluminum-rich melt in the system Al-Ni-Cu at 1100 K.

The enthalpy of the solution is determined by placing small amounts of nickel, copper, or both together into the final solution obtained in a preceding experiment, and measuring the enthalpy of this solution process. The measurements of h_i and the matching input weights of aluminum, nickel and copper are listed in Table 1. If there is a zero in the column for aluminum input weight, the sample was dissolved in the preceding solution.

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Table 1. MEASUREMENTS OF THE ENTHALPY OF SOLUTION, h, FOR <Ni> AND <Cu> IN (Al,Ni,Cu) AT 1100 K, WITH THE INPUT WEIGHTS.

Input weight in g			Enthalpy in
Al	Ni	Cu	Joules
31.9729	.2235	0	−530
0	.18254	0	−430
0	.14546	0	−346
0	.19995	0	−475.5
0	.20771	0	−490
0	.2064	0	−492
32.842	.15771	0	−364
0	.15256	0	−355.5
0	.17498	0	−405
0	0	.26216	−89
0	.16089	0	−370
0	.16864	0	−395.5
34.5082	.17249	0	−396
0	.1652	0	−378
0	.13311	0	−307.6
0	.16676	0	−386.5
0	.21167	0	−494
0	.1809	0	−424
39.601	0	.38974	−137
0	0	.46505	−165.5
0	0	.51815	−179
0	0	.56248	−194
0	0	.73841	−260
0	0	.989	−350.5
26.1662	.1775	0	−415
0	0	.1161	−41.2
11.52	.4801	0	−1118
0	0	.1156	−41.7
12.155	.5068	0	−1171
0	0	.0501	−17.5
25.1637	.3066	0	−720
24.9177	.2796	0	−656
0	.2492	.44684	−737
18.2003	.3662	.3194	−945
0	.4547	.3058	−1153.5

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Table 1. MEASUREMENTS OF THE ENTHALPY OF SOLUTION, h, FOR <Ni> AND <Cu> IN (Al,Ni,Cu) AT 1100 K, WITH THE INPUT WEIGHTS.

Input weight in g			Enthalpy in
Al	Ni	Cu	Joules
9.8397	.4964	.3568	-1270
0	0	.1493	----
0	.2654	0	-618.5
15.5693	.2921	.533	-863.5
0	.2647	.4234	-770
13.0043	.3341	.6183	-988
0	.3834	.8462	-1291
14.2102	.4049	.0339	-952.5
0	.1595	.0162	-377.5
27.3488	1.0517	1	-2402
0	0	.0176	----
0	.2447	0	-563
13.6921	.399	.0823	-952
26.5035	.8215	.1742	----
0	.2503	.0534	-602
0	.3105	.0589	-735

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The integral enthalpy H with respect to the elements at the measurement temperature is represented for this dilute solution by an aproximation polynomial [12]. The coefficients of the polynomial are determined by a computer from all the measurements by balancing calculations according to the usual Gauss method. Here the measurements are inserted as differential quotients from the difference Δh between the integral enthalpy of solution h and Δn (number of moles) for the added amount.

$$\frac{\Delta h}{\Delta n_i} \quad \frac{H_i(\Sigma n_{i,\text{vorher}} + \Delta n_i) - H_i(\Sigma n_{i,\text{vorher}})}{\Delta n_i} \qquad (2)$$

At the limiting transition $\Delta n_i \to 0$ the differential quotient becomes the relative partial molar enthalpy. /101
Without the limiting transition, which can be only approximated experimentally, the difference quotient (2) corresponds to the partial molar enthalpy of solution between initial and final concentrations of the meaqsurement, with the concentration not accurately defined. The polynomial obtained from the balancing calculation, therefore, is adapted to the H values for the dissolved materials.

In the range investigated here, for $x_{Ni} < 0.04$ and $x_{Cu} < 0.04$, it is sufficient to expand the polynomial to the second degree. the mean deviation of the measurements from the polynomial is 6 parts per thousand, and no value diverges more than 2%. The polynomial for the integral molar enthalpy of the diluted nickel-copper-

aluminum solution, referrred to <Ni>, <Cu> and (Al) at 1100 K is

$$\begin{aligned} \Delta H^L = & -136526\, x_{Ni} - 12769\, x^2_{Ni} \\ & - 22063\, x_{Cu} - 5777\, x^2_{Cu} \\ & - 96.6\, x_{Ni}\, x_{Cu}\ [\text{J/g-Atom}] \end{aligned} \qquad (3)$$

x_i is to be inserted as the mole fraction of component i.

The partial enthalpy of solution of nickel and copper in dilute Ni-Cu-Al solutions at 1100 K

The partial molar enthalpy ΔH_i for the component i is defined by

$$\Delta H_i \equiv \frac{\partial h}{\partial n_i} = \frac{\partial}{\partial n_i} \left[\left(\sum_j n_j \right) \Delta H \right] \qquad (4)$$

If this differentiation is rewritten in mole fractions and applied to the polynomial (3), then we get the following analytical expressions for the partial molar enthalpies if we neglect all the higher powers of x and the very small coefficient $C_{Ni\,Cu} = -96.6$:

ΔH_{Ni} in (Al) referred to <Ni> at 1100 K is (5)

$$\Delta H_{Ni} = -136.5 - 25.5\, x_{Ni} \pm 1.5 \text{ kJ/g-atom}$$

and ΔH_{Cu} in (Al) referred to <Cu> at 100 K is

$$\Delta H_{Cu} = -22.06 - 11.55\, x_{Cu} \pm 0.3 \text{ kJ/g-atom} \quad (6)$$

where x_i is always the mole fraction.

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Figure 2 shows the partial molar enthalpies for nickel and copper along with the measurements for the solutions containing only one element. The mean between the initial and final concentration for a solution process was chosen in each case as the concentration value for the measurement. With the low concentration dependence of both partial enthalpies in the range investigated, the choice of concentration is not critical.

The polynomials reported by Dannöhl and Lukas [12] for 1023 K and by Pool [20] for 1173 K are also included in the ΔH_{Ni}-x_{Ni} diagram. The values agree well within the reported errors. The difference can reflect the temperature dependence.

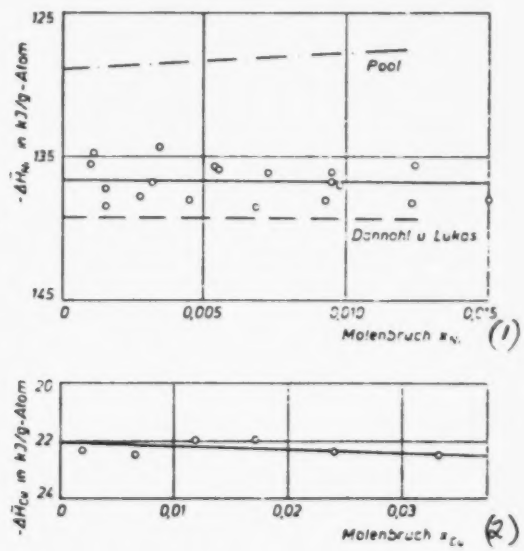

Figure 2. Partial molar enthalpies of solution ΔH_i of <Ni> and <Cu> in liquid (Al) at 1100 K.

1. Mole fraction x_{Ni} 2. Mole fraction x_{Cu}

The enthalpy of formation of the β phase of NiAl and (Ni,Cu)Al.

The enthalpy of solution h_i for each individual sample in liquid aluminum at 1100 K is determined from the calorimetric measurement. The amount of the aluminum solvent was chosen in each case so that the final solutions along a section with constant Ni/Cu ratio always had this same concentration. Thus the enthalpy of formation only linearly dependent on the reference state of the element. The curvature of $H^B(x)$, which is important only for the theoretical description of the phase, is then determined with the measurement accuracy given for $H^{1\cdots}$ and the accuracy of the alloy compositions.

Table 2 shows the values for the integral molar enthalpies of formation H^B referred to <Ni>, <Cu> and (Al) at 1100 K for alloys of the composition stated in each case. /102

Table 2. MEASURED INTEGRAL MOLAR ENTHALPIES OF FORMATION H° OF $(Ni,Cu)_{1-x}Al_x$ with x_{Ni}/x_{Cu} = ∞; 11; 5.

Mole Fraction			Enthalpy of formation	x_{Ni}/x_{Cu}
Al	Ni	Cu	kJ/g-atom	
0,42	0,58	0,0	−62,84	∞
0,43	0,57		−63,66	
0,44	0,56		−65,22	
0,45	0,55		−66,15	
0,46	0,54		−67,52	
0,47	0,53		−68,55	
0,48	0,52		−69,75	
0,48	0,52		−69,74	
0,49	0,51		−70,99	
0,49	0,51		−70,87	
0,50	0,50		−72,24	
0,50	0,50		−72,20	
0,51	0,43		−71,66	
0,51	0,49		−71,56	
0,52	0,48		−70,90	
0,53	0,47		−70,29	
0,54	0,46		−69,83	
0,400	0,550	0,050	−59,50	11
0,430	0,522	0,047	−62,99	
0,460	0,495	0,045	−66,17	
0,480	0,477	0,043	−67,65	
0,500	0,458	0,042	−68,29	
0,520	0,440	0,040	−67,56	
0,550	0,412	0,037	−65,88	
0,400	0,500	0,100	−58,33	5
0,430	0,475	0,095	−61,43	
0,460	0,450	0,090	−63,21	
0,480	0,433	0,087	−64,48	
0,500	0,417	0,083	−64,82	
0,520	0,400	0,080	−64,02	
0,550	0,375	0,075	−63,14	

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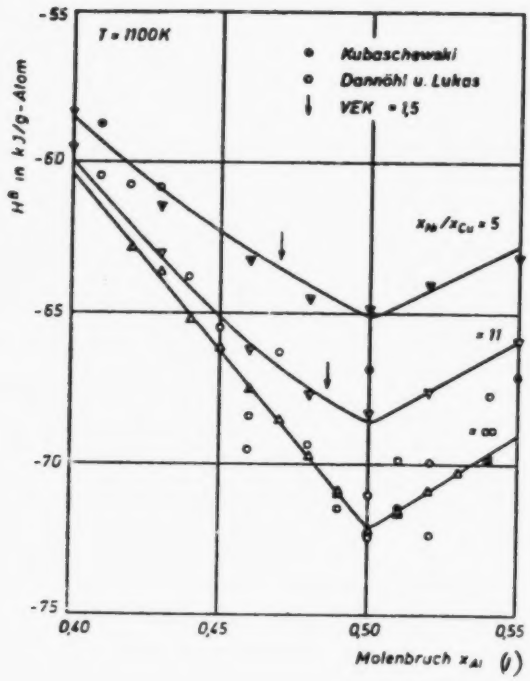


Figure 3. Integral molar enthalpy of formation, H^E for the phase $(Ni,Cu)_{1-x}Al_x$ with respect to <Ni>, <Cu> and (Al) at 1100 K on the sections $x_{Ni}/x_{Cu} = \infty$ (● according to Kubaschevski [11])(○ according to Dannöhl and Lukas [12]) (△ this work); $x_{Ni}/x_{Cu} = 11$ (▽); $x_{Ni}/x_{Cu} = 5$ (▼). Curves calculated from the Wagner-Schottky model with the coefficients shown in Table 3.

1. Mole fraction x_{Al}

The concentration of the final solution, and its enthalpy, was for: x_{Ni}/x_{Cu} = ∞ 1.40 atom-% Ni and -1916 J/gram-atom; for: x_{Ni}/x_{Cu} = 11 1.875 atom-% Ni, 0.17 atom-% Cu and -2603 J/gram-atom; and for x_{Ni}/x_{Cu} = 5 1.8972 atom-% Ni, 0.374 atom-% Cu and -2943 J/gram-atom.

The values of the enthalpy of formation H^F of the phase $(Ni,Cu)_{1-x}Al_x$ is plotted versus the aluminum concentration for the three sections in Figure 3. The two points at 55 atom-% are not part of the phase; metallographic testing showed heterogeneous alloys. The values of Dannöhl and Lukas [12] plotted in the figure were determined with an adiabatic solution calorimeter at 1023 K. They were not corrected to 1100 K because the correction is smaller than the variability. The values of Kubaschewski [11] are recalculated to the reference state <Ni> and (Al) at 1100 K selected here by means of the thermodynamic quantities for nickel and aluminum and the c_p value for NiAl according to Hultgren et al. [21]. All the values agree well together within the specified limits of error. The slopes, dH^F/dx agree in part. The most important quantity, d^2H^F/dx^2, the curvature of the curve of enthalpy as a function of the concentration, is for the first time established with satisfactory certainty through the values measured in this work.

Discussion

The curve of the measured enthalpy of formation (Figure 3) for copper-free β-NiAl can be described, to a very good approximation, by two straight lines. Therefore, the Wagner-Schottky model [1] is used to describe the thermodynamic quantities as functions of the

concentration, as the energy parameters in this model are independent of the concentration.

Table 3. COEFFICIENT SET FOR THE WAGNER-SCHOTTKY MODEL FOR THE PHASE (Ni,Cu)$_{1-x}$Al$_x$ AND THE REACTIONS DEFINING THE COEFFICIENTS.

Energy in kJ/g-atom	Vibrational Entropy in J/g-atom·K	Matching Reaction
$E = -72{,}15$	$S' = -16$	$\frac{1}{2}\langle Ni\rangle + \frac{1}{2}\{Al\} \rightarrow \frac{1}{2}\langle NiAl\rangle$
$E_{12} = 118$	$S'_{12} = 11$	$\langle Ni\rangle - \{Al\} \rightarrow Ni\|Al\|$
$E_{20} = 103{,}5$	$S'_{20} = 8$	$-\langle Ni\rangle \rightarrow \|Ni\|$
$E_{13} = 115$	S'_{13} } $S'_3 = S'_{23} - S'_{13}$	$\langle Cu\rangle - \{Al\} \rightarrow Cu\|Al\|$
$E_{23} = 83{,}6$	S'_{23} } $= 34$	$\langle Cu\rangle - \langle Ni\rangle \rightarrow Cu\|Ni\|$
$E_0 = 180{,}7$	$S'_0 = -5$	$o \rightarrow NiAl + Ni\|Al\| + 2\|Ni\|$
$E'_0 = -86{,}6$	$S''_0 = -45$	$o \rightarrow Cu\|Al\| - Cu\|Ni\| - Ni\|Al\|$

The energy and the lattice vibration portion of the entropy are used here as linear combinations of the concentrations of the individual lattice structural elements. The matching coefficients, E_{ij} and S'_{ij}, are the energy of formation and entropy of formation of the individual lattice structural elements referred to the pure elements <Ni> or {Al}. They are listed in Table 3 along with the matching reaction equations. With the lattice structural elements considered here (<NiAl> normally occupied lattice sites; NiAl Ni atom at Al site; Ni Ni vacancy site; CuAl, Cu atom at Al site;

CuNi, Cu atom at Ni site) the energy per gram-atom becomes:

$$E = E^{\bullet}(1+x_{20}) + E_{12}\cdot x_{12} + E_{20}\cdot x_{20} + E_{13}\cdot x_{13} + E_{23}\cdot x_{23} \qquad (7)$$

The $x_{i,j}$ are the concentrations of atom of type j in lattice sites of type i. The zero symbolizes a vacancy site. $E^{\bullet}$ is the energy of formation of a gram-atom of ideally ordered stoichiometric phase. The concentrations are referred to 1 gram-atom of input weight (without vacancy sites). Therefore, there are $1 + x_{20}$ lattice sites present.

For the vibrational entropy, analogously:

$$S^{v} = S^{v\bullet}(1 + x_{20}) + S^{v}_{12}\, x_{12} + S^{v}_{20}\, x_{20} + S_{13}\, x_{13} + S_{23}\, x_{23} \qquad (8)$$

The configurational entropy is represented in this model by the ideal mixing term:

$$\begin{aligned} S^{konf} = & \\ -R\Big\{ & x_{12}\ln x_{12} + x_{13}\ln x_{13} + (1-x_{12}-x_{13})\ln(1-x_{12}-x_{13}) \\ & + x_{20}\ln x_{20} + x_{23}\ln x_{23} + (1-x_{20}-x_{23})\ln(1-x_{20}-x_{23}) \\ & - (1+x_{20})\ln\left(\frac{1+x_{20}}{2}\right)\Big\} \end{aligned} \qquad (9)$$

The last term considers that $\frac{1+x_{20}}{2}$ gram-atoms of lattice sites are available for distribution on each of the partial lattices.

With constant nickel and copper concentration, then of the four quantities $x_{1,2}$, $x_{2,0}$, $x_{1,3}$ and $x_{2,3}$, only two are independent, because they must satisfy the secondary conditions:

$$\frac{1 + x_{20}}{2} - x_{12} - x_{13} - x_1 \triangleq x_{A1} \qquad (10)$$

$$x_{13} + x_{23} = x_3 \triangleq x_{Cu} \qquad (11)$$ 103

At thermodynamic equilibrium the $x_{i,j}$ as internal parameters adjust themselves to that the free enthalpy G of the phase is at a minimum with respect to the variations of these quantities.

This minimal condition for G can be written in the form of two mass action equations:

$$\frac{8 \cdot x_{12} \cdot x_{20}^2}{(1 + x_{20})^2 (1 - x_{20} - x_{23})} = K_n = \exp\left(\frac{-E_o}{RT} + \frac{S_o^v}{R}\right) \qquad (12)$$

and

$$\frac{x_{13} \cdot (1 - x_{20} - x_{23})}{x_{12} \cdot x_{23}} = K_o' = \exp\left(\frac{-E_o'}{RT} + \frac{S_o^{v'}}{R}\right) \qquad (13)$$

The corresponding reaction equations are those linear combinations of the definition equations for the coefficients which yield the reference states of the pure elements, {Al}, <Ni>, and <Cu>. The coefficients E_o,

$S^{v}_{\bullet\bullet}$, $E'_{\bullet}$ and $S^{v\prime}_{\bullet}$ are the analogously formed linear combinations of the coefficients $E_{i,j}$ or $S_{i,j}$:

$$E_{\bullet} = 2E^{\circ} + E_{12} + 2E_{20},\ S^{v}_{\bullet} = 2S^{v\circ} + S^{v}_{12} + 2S^{v}_{20} \tag{14}$$

$$E'_{\bullet} = E_{13} - E_{23} - E_{12},\ S^{v\prime}_{\bullet} = S^{v}_{13} - S^{v}_{23} - S^{v}_{12} \tag{15}$$

They are shown, along with the corresponding reaction equations, at the bottom of Table 3.

The coefficients were calculated from the measurements using a balancing computation according to Gauss. In the computation, a set of approximate values for the coefficients was first entered, and from those, theoretical values were formed for the measured function values and their derivatives with respect to the coefficients (partial derivatives in the directions allowed by Equations (10) through (13)). These were then summed as usual in the matrix of the Gaussian standard equations. We used as measurements not only our own enthalpy values but also the partial molar free enthalpies of aluminum measured by Steiner and Komarek [10].

As the measurements M(x,T) are of differing quality, a weight was assigned to each M. It is essentially the square of the reciprocal of the estimated mean error ΔM. Naturally, the measurement is also undetermined in the variables x and T. This uncertainty Δx is recalculated into an error of M according to the equation

$$\Delta M_x = \frac{\delta M(x,T)}{\delta x} \cdot \Delta x \tag{16}$$

and also for T. The total weighting factor p for a measurement is then $p = 1/(\Delta M^2 + \Delta M_x^2 + \Delta M_T^2)$

The calculation was done first for the copper-free phase $Ni_{1-x}Al_x$. From the six coefficients introduced, the two coefficients E_0 and S^v_0, which alone determine the disorder equilibrium of the phase, can be calculated from Equation (14). These two coefficients are determined with the accuracy of the measurements.

But real measurements always include reference states. therefore it is reasonable for the calculation also to define the coefficients so that they contain the reference states. For comparison with thermodynamic functions of other phases the added information of the reference state is important, and the calculation of heterogeneous equilibria is based on such comparisons. For these reasons, all six coefficients are calculated here.

The available measurements give only five of the six coefficients used. The three enthalpy coefficients are determined by the measurements of the enthalpy of formation. The μ_{Ni} values according to Steiner and Komarek [10] determine only two more linearly dependent combinations of the three vibrational entropy coefficients, as the course of the μ_{Ni} curve must be invariant with respect to a variation of the reference state for nickel. Therefore, measurements of the Debye temperature by Hughes et al. [22] were used for one further determining equation. A value for the vibrational portion of the entropy of the ideally ordered

stoichiometric phase can be obtained by integration of the Debye function for the specific heat. Through comparison of the values of the entropies of the pure elements (Al) and <Ni> tabulated by Hultgren et al. [21], the entropy of formation of the stoichiometric phase is found to be $S^{\circ\circ}$ = -16 J/g-atom·K.

The Wagner-Schottky model requires the inflection of the activity or μ curve at the stoichiometric composition. Therefore, Libovitz [14] had to shift the measurement of Steiner and Komarek [10] to higher aluminum contents. This is also justified because Ettenberger, Komarek and Miller, in a later work [8] on PbAl, themselves undertook such a concentration correction, and the same procedure was used for the analysis of NiAl samples [10]. For that reason, the original values of Steiner and Komarek [10] were also here displaced toward higher aluminum contents by 1.2 atom-%, corresponding to Libovitz [14].

Now, with the specified value for $S^{\circ\circ}$, the remaining five coefficients can be determined from the enthalpy values and the μ values by the Gauss method presented. The set of coefficients obtained in that way is shown in Table 3.

The distribution into the individual coefficients is, again, given only with the accuracy of the measurements, and especially those of the Debye temperature [22]. With the coefficient set given, all the thermodynamic functions of the β-phase $Ni_{1-x}Al_x$ can be calculated as functions of the concentration and the temperature.

In Figure 3, the enthalpy of formation calculated with these coefficients is plotted by computer as a function of the concentration at 1100 K with the measurements determined at that temperature. Figure 4, likewise, shows a computer plot of the molar free enthalpy of aluminum determined with the same coefficients as a function of the concentration for 1323 K, using the measurements of Steiner and Komarek [10] corrected in the manner described above. The plane representation requires conversion of the μ values determined at different temperatures. Therefore, the μ values are recalculated to 1323 K by means of the model. The left branch of the curve could be described better by a concentration-dependent parameter $S^{v}_{i,i}$. This is hard to imagine with constant $E_{i,i}$, so that this possibility was not followed up in consideration of the variation of the μ values.

The H curve in particular, but also the μ curve which was calculated with the same coefficients, reproduce the actual measurements very well. The Wagner-Schottky model with its simple prerequisite of concentration-independent parameters is also quite capable of describing all the thermodynamic measurements known so far for the phase /104 $Ni_{1-x}Al_x$, even for large deviations from stoichiometry.

The enthalpy says practically nothing about the slight inherent defect structure existing here. Its contribution to the energy at 1100 K is always less than 100 J/g-atom. Therefore the enthalpy coefficients of the Wagner-Schottky model can be assigned to the enthalpy curve as in Figure 3 in geometrically visible manner. As the equilibrium constant K_s is very small, it follows

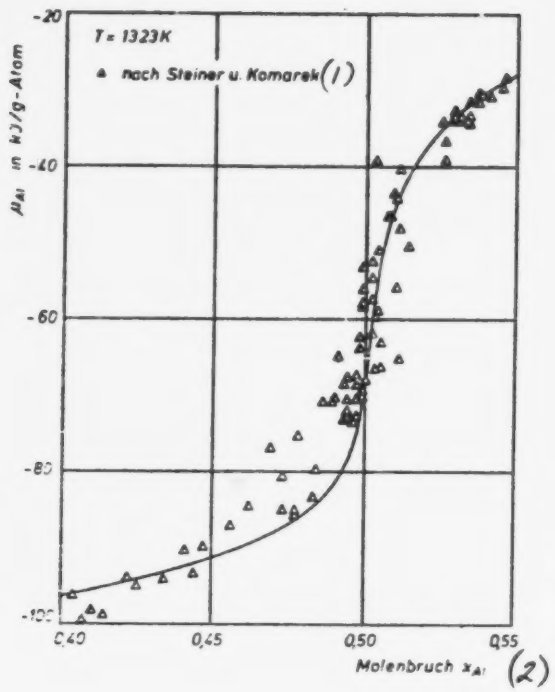


Figure 4. Partial molar free enthalpy of aluminum, μ_{Al}, in the phase $Ni_{1-x}Al_x$ calculated from the Wagner-Schottky model with the coefficient set according to Table 3 for 1323 K. Corrected measurements from Steiner and Komarek [10].

1. according to Steiner and Komarek.
2. Mole fraction x_{Al}

from Equation (10) for $x_{12} = 0$ that only one of the two concentrations, x_{20} or x_{12} can reach a significant amount and then depends practically linearly on the aluminum concentration and certainly

(17)

$$x_{Ni} \cong \frac{1}{2} - x_{Al}, \quad x_{Ni} \cong 0 \quad \text{for } x_{Al} < 0{,}5$$

$$x_{Ni} \cong 2x_{Al} - 1, \quad x_{Al} \cong 0 \quad \text{for } x_{Al} > 0{,}5$$

(18)

Then it follows from Equation (7), if one equates the enthalpy with the internal energy, that the slope of the left part of the enthalpy curve for the copper-free phase in Figure 3 is equal to $-E_{te}$, and that of the right part is equal to $2(E^{\bullet} + E_{ee})$. The difference in the slopes is equal to the coefficient $E_{\bullet}$, which again makes it clear that this coefficient is independent of the reference state.

The linearity of both branches of the enthalpy curve confirms, with great accuracy, the constancy of the enthalpy coefficients. The refined models mentioned in the introduction would essentially have to reduce to the predictions of the Wagner-Schottky model, which they contain as a limiting case. That means that the parameters which describe the concentration dependence become zero or vanishingly small in comparison with the parameters that can be separated out as independent of the concentration. Therefore it is not necessary [line(s) missing in text] these refined [missing].

In the application of the Gauss method to the copper-substituted phase $(Ni,Cu)_{1-x}Al_x$ the six coefficients determined from the copper-free phase were assumed to be known, as they are independent of concentration by definition. The two additional enthalpy coefficients can next be determined from the measured enthalpy values.

But the entropy coefficients also affect the enthalpy because they influence the equilibrium values for the internal parameters, so that the factors $x_{i,j}$ change the individual energy parameters in Equation (7). But these factors are affected only by the difference of the two entroppy parameters, because the concentrations $x_{1,3}$ and $x_{2,3}$ depend only on this difference, according to Equations (13) and (15).

The calculated parameters, $E_{1,3}$, $E_{2,3}$, $S^v_{1,3}$, and $S^v_{2,3}$, and the paremeters defined by them, $E'_{\bullet}$ and $S^{v\prime}_{\bullet}$, are given in Table 3. With the set of coefficients obtained, any selected thermodynamic functions can be calculated as functions of the concentration and the temperature.

Figure 3 shows the enthalpy of formation, calculated with this set of coefficients, as a function of the aluminum concentration also for the two sections with constant Ni/Cu ratio, along with the measurements. The agreement shows that the Wagner-Schottky is basically capable of describing this ternary disorder structure also.

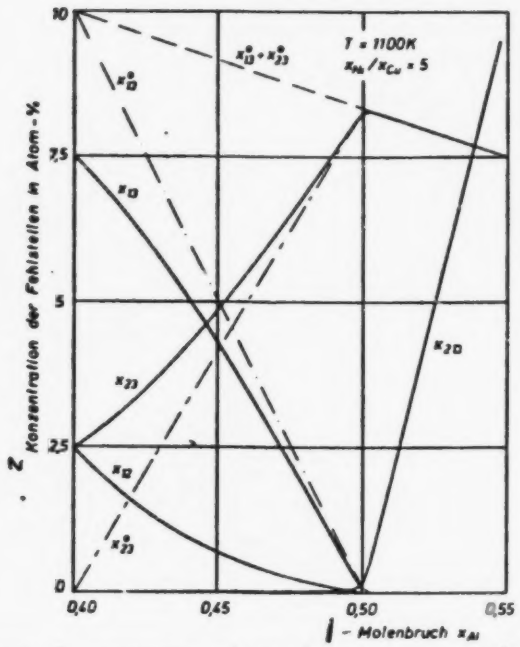
The somewhat less good agreement of theory and experiment in the ternary case, compared with the agreement in the binary case, could have the following causes:

he concentration of the final solution in the enthalpy measurement is naturally constant only for the individual steps with constant Ni/Cu ratio. It must change from curve to curve.

The accuracy of the enthalpy coefficients determines the relative position of the curves; but these coefficients

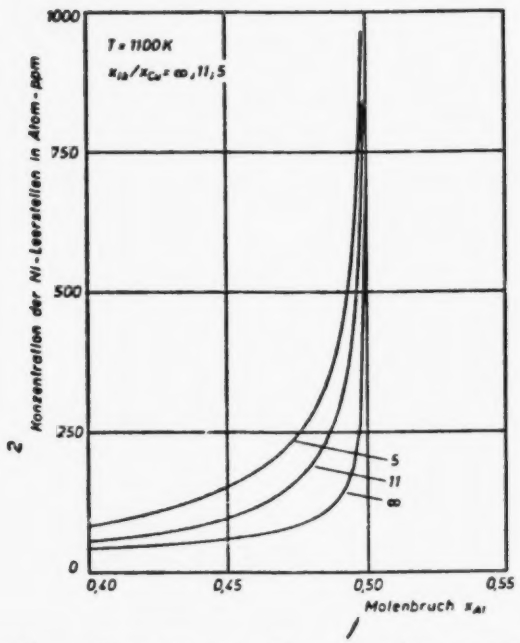
cannot be more accurate than the enthalpy of the dilute solution of nickel and copper in aluminum, which represents the major contribution to the enthalpy of formation.

As the (Ni,Cu) Al phase is a ß-Hume-Rothery phase, the contribution of the electron gas to the energy must eventually be considered more strongly, as by Jacobi and Engell [16]. To a first approximation, we can assume a sudden change of an energy coefficient of the electrons at the concentration at which the Fermi body contacts the Brillouin zone. This must appear as a sharp bend in the integral enthalpy curve. For the copper-free alloys the critical VEK $\cong$ 1.5 is reached at the stoichiometric composition. Therefore a possible discontinuity in the curve for the enthalpy of formation may remain concealed in the bend of the curve (Figure 3). With increasing exchange of Ni for Cu, the concentration at which the critical VEK $\cong$ 1.5 is reached shifts to lower aluminum contents. This concentrations is indicated in Figure 3 by arrows for the two curves for copper-containing alloys. Here, splitting out of the electronic term is theoretically possible; but it was not attempted because of the small number of measurements.



1--mole fraction; 2--vacancy sites in atom, concentration %

Figure 5. Concentration of the nickel vacancy sites $x_{2\square}$, the nickel anti-structure atoms x_{12}, and the copper in the aluminum sublattice x_{13} and in the nickel sublattice x_{23} of the phase $(Ni,Cu)_{1-x}Al_x$ on the section $x_{Ni}/x_{Cu} = 5$, calculated from the Wagner-Schottky model with the coefficient set from Table 3.



1--mole fraction; 2--vacancy sites in atom, concentration %

Figure 6. Nickel vacancy site concentrations in the phase $(Ni,Cu)_{1-x}Al_x$ calculated from the Wagner-Schottky model with the coefficient set of Table 3 for 1100 K, with the replacement ratios x_{Ni}/x_{Cu} = ∞; 11; 5.

Figure 5 shows the calculated vacancy concentrations with respect to the total number of atoms for the section x_{Ni}/x_{Cu} = 5 plotted vs. the aluminum concentration. As indicated previously for the calculation of the coefficients, these concentrations are directly matched to the experiment through their effect on the /105 course of the enthalpy curves. The auxiliary lines plotted are intended to show the course of the equilibrium at lower temperatures. If the temperature

approaches 0 K, then the inherent disorder (thermal disorder) becomes zero. Also, the equilibrium for the copper distribution over the two sublattices for the aluminum-poor alloys is such that all the copper is inserted into the aluminum sublattice; and for the aluminum-rich alloys, such that all the copper is built into the nickel sublattice. Advancing in the direction of increasing aluminum content this would mean that first the nickel is removed from the aluminum sublattice along the lines of $x^{\circ}_{1,2}$. Beyond the aluminum concentration of $x_{A1} = 2/5$ determined from the ratio $x_{N1}/x_{C1} = 5$, copper would be removed from the aluminum sublattice along the line $x^{\circ}_{1,2}$ and built into the nickel sublattice corresponding to the line $x^{\circ}_{2,2}$. At the composition $(Ni+Cu)_{0.5}Al_{0.5}$ the aluminum sublattice is completely occupied by aluminum.

Corresponding to the assumption of no aluminum antistructure atoms, a further increase of the aluminum concentration is possible only through formation of nickel vacancies along a line x°_{20}. This is not plotted in the figure, as it is largely coincident with the curve x_{20}.

he influence of the temperature over the entropy on the distribution of copper in the nickel and aluminum sublattices increases the copper concentration in the nickel sublattice x_{22} with increasing temperature, and correspondingly reduces the copper concentration in the aluminum sublattice. Corrresponding to this reduction, the concentration of nickel antistructure atoms, x_{12}, increases. The concentration of the nickel vacancy sites, x_{20}, is only slightly affected by the substitution

of nickel by copper on the aluminum-rich side, as shown by comparison of the $x_{v_{Al}}$ curves in Figure 6 for the three different Ni/Cu ratios. The vacancy site concentration and its dependence on the copper content is clearly lower than the value determined by Jacobi and Engell [15] by comparison of pycnometer and X-ray densities. As the applicable equilibrium temperature cannot be determined accurately in these measurements, and sample porosity cannot be completely ruled out, the values cannot be compared directly.

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List of abbreviations

1	$\overline{JG}_i = \mu_i$	partial molar free enthalpy of component i
2	H^B, H^L, H^M	integral molar enthalpy of formation, solution and mixing
3	$\overline{JH}_i$	partial molar enthalpy of component i
4	· = 1 ≙ Al, 2 ≙ Ni, 3 ≙ Cu, 0 ≙	vacancy sites
5	x_i	mole fraction of component i
6	( )	solid
7	{ }	liquid
8	$[A]_B$	A dissolved in B
9		according to O. Kubaschevski
10	Cu|Al|, Cu|Ni|	Cu at Al-(Ni) site
11	Ni|Al|	Ni at Al site
12	|Ni|	Ni vacancy site
13		new Schottky notation
14	$E^{\cdot}, S^{\cdot}$	energy (entropy) parameter of the Wagner-Schottky theory for 1 gram-atom of ideally ordered alloy
15	E_{ij}, S^v_{ij}	energy (entropy) parameter for the formation of 1 gram-atom of vacancy sites for the atom j in the sublattice i. /106
16	x_{12}	concentration of the Ni antistructure atoms
17	x_{13}, x_{23}	concentration of the Cu atoms in the Al-(Ni) sublattice
18	x_{20}	concentration of the Ni vacancy sites
19	$x^0_{ij}, x^0_{12}, x^0_{20}$	concentration without inherent disorder
20		referred to the total number of atoms

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